

AMENDED SPECIFICATION

This print embodies amendments in accordance with the Decisions of the Superintending Examiner acting for the Comptroller General, dated the first day of November, 1961, under Section 14 of the Patents Act, 1949, and the twentyseventh day of April, 1961, under Section 29.

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Production of High Molecular Weight Polyethylenes

I, KARL ZIEGLER, a citizen of the Federal Republic of Germany, of 1, Kaiser Wilhelm Platz, Mulheim/Ruhr, Germany, do hereby declare the invention, for which I pray that

5 a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the production of high molecular weight polyethylenes that is ethylene polymers with molecular weights of over 2,000 and preferably over 10,000, which are suitable for use as synthetic material or plastic.

15 In general there may be obtained in accordance with the invention by the use of appropriate catalyst mixtures, polyethylenes of a molecular weight in excess of that hitherto regarded as the upper limit for industrially produced polyethylenes. Thus the invention enables the production of polyethylenes of molecular weights above 50,000 determined as set out below from viscosity values of solutions of the polyethylenes. The viscosity value, i.e.

20 25 30 being corrected according to Fox, Fox and Flory (Journal of the American Chemical Society, 73 (1951) page 1901). The average molecular weight of 50,000 referred to above is calculated from this intrinsic viscosity with

35 the aid of a converted form of the formula (5) described by R. Houwink in Journal für Praktische Chemie, New Series, 157, (1940), pages

15—16: Mol.Wt. = $K(\eta)^a$, wherein for the new polymers, the constants K and a were calculated to be $2.51 \cdot 10^4$ and 1.235 respectively. Molecular weights referred to in connection with the products of the invention, including those in the examples given later, are the molecular weights derived in this fashion from viscosity determinations. In the sense of such a definition of molecular weight, polyethylenes of molecular weights of up to 3,000,000 and higher are obtainable in accordance with the invention by the choice of suitable catalyst combinations and concentrations.

40 45 50 55 60 65 70 The polyethylenes produced according to the invention are, as already indicated, of exceedingly high molecular weight. They have a softening point or melting point of above 130°C. They are completely insoluble at room temperature in all solvents. Of these polyethylenes, those having the lower molecular weights (up to a molecular weight of about 100,000) dissolve partially first at temperatures in excess of 70°C. Those of higher molecular weight (with a molecular weight above 100,000) dissolve partially first at temperatures above 100°C. The temperature stability of the new products is greater than that of the known polyethylenes. On heating the new products to temperatures above 250°C they retain their white colour whilst the colour of the known products changes to grey between 200 and 250°C. The resistance of the new products to oxidation by atmospheric oxidation is likewise greater.

The new polyethylenes have a highly crystalline structure which is most unusual for high molecular weight hydrocarbons. The crystal-

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larity remains unaltered up to over 100°C and disappears only at a temperature close to the softening point.

5 The degree of crystallinity, as Rontgen ray diagrams show, generally amounts to about 80% and is often higher. Naturally lower values are also obtained.

10 Chemically, the products exhibit a fully linear structure and possesses practically no branched chains. The products of the invention possess at the most three methyl groups for every hundred methylene groups. In general the proportion of methyl groups is appreciably less than this and amounts to at most 0.03% and often is below 0.01%. Infra red spectrum photographs of the products do not show, in contrast with the known polyethylenes, any characteristic methyl bands.

15 20 The tear strength (Zerreissfestigkeit) is at least 100 kg/cm², and often over 200 kg/cm². The tensile strength (Zugfestigkeit) in the un-stretched condition is greater than 200 kg/cm² and is up to 3,000 kg/cm² for foils orientated by stretching.

25 30 The products may be directly formed into clear, transparent, elastic and flexible sheets or foils. They are also suitable for working up in extrusion presses or by the injection moulding process. They are stretchable in the cold and may in this way be drawn out into strips, threads or filaments of high elasticity and strength, which has not yet been achieved with polyethylenes produced in the known manner. The products exhibit even during the working up a noticeable inclination to fibre formation. They can be spun in the molten state to filaments by the methods usually employed in the spinning of superpolyamide filaments such as nylon filaments. The filaments formed from the new polyethylenes can be used as fibres for industrial purposes.

35 40 Previously polyethylene has been produced by the known high pressure process in which very high pressures—in practice 1,000 atm. and more—are used, and which is usually carried out in the presence of oxygen or peroxides as polymerisation initiators. According to one known process metals and organic halides which yield reagents of the Grignard type are used as catalysts if required together with oxygen as catalyst. Thus magnesium and zinc and alkyl halides have been proposed for such catalysts.

45 50 55 It has now been found that particularly effective catalyst combinations, which effect an exceptionally rapid polymerisation of gaseous ethylene even at low pressures to polymerisates of the type mentioned in the introduction of this specification and having high molecular weights of over 2,000 are obtained by mixing organic compounds of magnesium and/or zinc with salts of the metals of sub-groups α of Groups IV to VI of the Periodic Table, including thorium and uranium.

The invention consists in a process for the production of high-molecular weight polyethylenes in which gaseous ethylene is brought into contact with a product formed by mixing an organo-metallic compound selected from the organic compounds of magnesium and the organic compounds of zinc, with a compound of a metal of the α sub-groups of Groups IV to VI of the Periodic Table, including thorium and uranium, the choice of constituents and the conditions of mixing being such as to yield an effective ethylene polymerising catalyst.

60 65 70 75 The formation of catalysts effective for polymerising ethylene to high molecular weight polymers, involves mixing two classes of constituents. The first of these classes is defined as organo compounds of magnesium or zinc, and the second of these classes must be a compound of a metal of the α sub-groups of Groups IV to VI of the Periodic Table including thorium and uranium. While it is believed that these classes properly define the constituents suitable for the end purpose in view, there remains a possibility of isolated cases in which a particular member of the first class, when mixed with a particular member of the second class under the conditions described and illustrated hereafter, does not yield a catalyst for the polymerisation of ethylene to high molecular weight polymers. By following the directions herein set forth and illustrated in the Examples, it is believed however that these will afford ample guidance to those skilled in the art on the production of effective catalysts, that is, effective for the conversion of ethylene to high molecular weight polyethylene, under the conditions of operation set forth herein.

80 85 90 95 100 105 As organo-metallic compounds there may be used in the process of the invention magnesium alkyls and aryls and zinc alkyls and aryls, for example, magnesium or zinc dimethyl, diethyl, dipropyl, dibutyl or even higher alkyls. However, organic compounds of magnesium or zinc may also be used in which only one valency of the metal is attached to a hydrocarbon radical, the other being bound to a halogen, that is, Grignard compounds or the corresponding zinc compounds. In these compounds the hydrocarbon radical may be either aliphatic or aromatic in nature.

110 115 120 125 The organic compounds of magnesium and zinc used in forming the products for use as catalyst in the present invention are, in varying degrees, unstable when exposed to the air and this circumstance in itself apart from other factors, requires that the catalyst be formed by mixing a magnesium or zinc compound and a compound of a metal of the α sub-groups of Groups IV to VI of the Periodic Table including thorium and uranium, under conditions which exclude contact with the atmosphere e.g. in an inert atmosphere such as nitrogen.

The organic compounds of zinc or mag-

- nesium are used with compounds of the metals of sub-groups α of Groups IV to VI of the Periodic Table, including thorium and uranium. So, for example, compounds of 5 titanium, zirconium, hafnium, thorium, uranium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten may be used. Particularly advantageous are salts of titanium, zirconium or chromium. Suitable 10 compounds of the mentioned metals are halides, e.g. chloride and bromide; oxyhalides, e.g. oxychloride; complex halides, e.g. complex fluorides; and freshly precipitated oxides, hydroxides and organic compounds e.g. alk- 15 oxides, acetates, benzoates and acetyl acetones. A particularly effective catalyst for for use in the invention is obtained if, for example, titanium or zirconium tetrachloride, oxychloride or acetyl acetone is mixed with 20 organic magnesium or zinc compounds. Such a catalyst converts ethylene, even at low pressures of under 100 atm. and at temperatures below 100°C., very rapidly into high molecular weight polyethylene.
- 25 The known high pressure processes have the further disadvantage that in an operational cycle only a relatively small amount of about 15–20% of the ethylene introduced is converted to polyethylene. In contrast therewith 30 in the process of the invention the introduced ethylene is largely converted in a single operational cycle. Furthermore, the ethylene used in the process of the invention need not be of the purity required for the known processes.
- 35 The polymerisation process of the invention can be carried out at pressures below 250 atmospheres, and at the relatively low pressures of 10–100 atm. It can also be carried out at pressures of less than 10 atm. and indeed at 40 atmospheric or sub-atmospheric pressure. Naturally, the action of the new catalyst on the ethylene remains basically the same when the pressure is increased to any degree technically possible.
- 45 The polymerisation catalysts described are almost all active at room temperature and below. It is advantageous, however, to operate at elevated temperatures, particularly above 50°C. Working at temperatures above 250°C. 50 is not desirable since the catalyst decomposes extensively at this temperature.
- Ethylene containing mixtures may be treated directly in place of pure ethylene by the process of the invention. For example, gases may 55 be used which are produced in the cracking of saturated hydrocarbons, e.g. ethane and propane, or of petroleum and its fractions, or in the Fischer-Tropsch Synthesis, and which, if necessary, have been freed from other olefins.
- 60 Polymerisation is conveniently effected in the presence of an inert organic solvent. The latter must not promote the dissociation of the metal compounds. For this reason water, methanol and other solvents with high dielectric constants do not come into question. Such
- solvents break down the organic compounds of magnesium or zirconium. Inert solvents in which the metal salts are insoluble and do not dissociate, may be used. As such are suitable aliphatic and hydroaromatic hydrocarbons, e.g. pentane, hexane, cyclohexane, tetrahydro-naphthalene, decahydronaphthalene and higher paraffins which are liquid at the reaction temperature; aromatic hydrocarbons, e.g. benzene and xylene; halogenated aromatic hydrocarbons, e.g. *o*-dichlorbenzene or chlorinated naphthalene; and ethers e.g. dibutyl ether, dioxane and tetrahydrofuran. In working with Grignard compounds it has been shown to be preferable when using ethers as solvents to remove these as completely as possible before the addition of the heavy metal compounds. The solvents are used in at least such quantities that stirring of the reaction mixture is still possible towards the end of the reaction. In general it is still possible to stir when the reaction mixture contains from 10–40% of polyethylene. The above limits are solely related to the economics of the process.
- The invention is illustrated by the following examples.
- EXAMPLE 1.**
- 2 g. of titanium tetrachloride are dissolved in 50 ccm. of hexane and 3.5 g. of solid dimethyl magnesium are added to the solution under an atmosphere of nitrogen. The whole is transferred under nitrogen to a small ball mill and vigorously ground for 1 hour. The contents of the ball mill are then transferred under nitrogen to an autoclave of 200 ccm. capacity and the ball mill itself washed with 25 ccm. of additional hexane. Ethylene at 70 atm. pressure is then introduced into the autoclave and the latter is shaken. The autoclave heats spontaneously up to about 50°C. and the ethylene pressure drops. Ethylene is introduced a further three times until a total of 30 g of ethylene has been introduced into the autoclave. Finally the autoclave is shaken for some hours until the pressure therein has dropped to a small residual amount. The contents of the autoclave then consist of a solid cake of agglomerated polyethylene particles which is permeated with the solvent. The cake can easily be removed from the autoclave. The cake is kneaded with methanol, then with methanolic hydrochloric acid and washed with methanol and dried. A white polymer is thus obtained which is insoluble, or at most swells, in the usual solvents, and softens between 150 and 200°C. It may satisfactorily be pressed to a clear foil at 170°C.
- The polyethylene produced in this example had an intrinsic viscosity of 9.6 corresponding to a molecular weight of about 400,000. By increasing the ethylene pressure during the polymerisation to 240 atmospheres, a polyethylene of molecular weight of about 3,000,000 is obtained.
- In this example, the ethylene may be intro-

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duced at a pressure lower than that quoted and the polymerisation may be carried out at low pressures or even by simply passing the ethylene through the catalyst mixture.

EXAMPLE 2.

A solution of 35 g. of chromium acetyl acetonate in solution in a quantity of xylene just sufficient for solution is allowed to run under nitrogen into a warm Grignard solution of 24 g. magnesium, 94 g. butyl chloride and 500 ccm. ether. A reaction takes place with vigorous boiling off of the ether and with a darkening in colour of the mixture. This mixture is an advantageous catalyst for the polymerisation of ethylene.

EXAMPLE 3.

24.6 g. of diethyl zinc is mixed with 6 g. of finely powdered water-free zirconium tetrachloride and the mixture warmed until the particles of zirconium tetrachloride in suspension have completely disappeared. 200 ccm. of benzene are then added, always under nitrogen, the whole is introduced into a 500 ccm. autoclave and treated in the manner described in example 1 with ethylene. The ethylene is rapidly taken up and there separates in the autoclave a swollen jelly-like mass of polyethylene which is first kneaded with methanol and thereupon freed from the solvent by a steam distillation in the presence of ordinary hydrochloric acid. The polyethylene remains suspended in the aqueous phase in the form of pure white grains. The yield of polyethylene is practically quantitative. Its intrinsic viscosity was 14.9, which corresponds to a molecular weight of about 700,000.

EXAMPLE 4.

To a Grignard solution of 157 g. of bromobenzene and 24 g. of magnesium in 500 ccm. ether. 42.5 g. of *o*-titanic acid tetrabutyl ester — $Ti(OC_4H_9)_4$ — are added under nitrogen dropwise at the temperature of boiling, and this is followed by heating for a further hour with gentle boiling. As much ether as possible is distilled off on a bath heated to 50°C. and the remaining mixture is introduced under nitrogen into an autoclave of suitable size. Ethylene is now introduced at about 50 atm. pressure and the whole is heated to about 100°C., whereby the ethylene is rapidly polymerised. Further ethylene can be introduced a number of times before the catalyst finally becomes ineffective in its action due to its becoming coated with the polymer which separates out. The working up follows as described in the preceding examples. The polyethylene obtained is similar to the products which can be obtained with titanium tetrachloride and Grignard compounds. The polyethylene had an intrinsic viscosity of 7.2, i.e. it had an average molecular weight of about 280,000.

EXAMPLE 5.

A solution of propyl magnesium chloride is produced in the usual manner from 24 g. of

magnesium and 78 g. of *n*-propyl chloride in 500 ccm. ether and this solution is allowed to flow into one litre of boiling toluene whilst stirring. The toluene is contained in a distillation apparatus fitted with a column and with an effective stirrer. The ether is distilled off with vigorous stirring of the mixture and so much toluene is allowed to follow until the refractive index of the distillate has again reached exactly the value valid for toluene. During this operation the propyl magnesium chloride precipitates out as a fine insoluble precipitate in the toluene. The volume of the suspension should again be about 500 ccm. at the end of the operation. If necessary, further toluene is added during the distillation. The suspension finally obtained may suitably be ground for some hours in an oscillating ball mill. 25 ccm. of this suspension of propyl magnesium chloride in toluene are then carefully mixed under nitrogen with 1.9 g. titanium tetrachloride and ground in a small oscillating ball mill. The resultant, now darkly coloured, suspension is mixed with 1 litre of a fully saturated, dried and air-free Fischer-Tropsch diesel oil and thereupon ethylene is introduced in the absence of air whilst stirring. Heating to a temperature of 60—70°C. takes place. The ethylene is immediately absorbed and the separation of flocculent polyethylene commences very soon. The speed at which the ethylene is taken up can be increased if the ethylene pressure is increased to about 10 atm. The introduction of ethylene is continued until the stirrer sticks fast. At this point about 200—250 g. of polyethylene have separated out. The polyethylene had an intrinsic viscosity of 10.4, corresponding to a molecular weight of about 450,000.

The solid polyethylenes of high molecular weight produced by the foregoing Examples 1 to 5 have the following properties:

- (i) less than 1 methyl group per 500 methylene groups,
- (ii) melt or soften above 130°C.,
- (iii) are insoluble in the usual organic solvents at atmospheric temperatures,
- (iv) have a tear strength not less than 100 Kg./cm.².

WHAT I CLAIM IS:—

1. A process for the production of high-molecular weight polyethylenes in which gaseous ethylene is brought into contact with a product formed by mixing an organometallic compound selected from the organic compounds of magnesium and the organic compounds of zinc, with a compound of a metal of the *a* sub-groups of Groups IV to VI of the Periodic Table, including thorium and uranium, the choice of constituents and the conditions of mixing being such as to yield an effective ethylene polymerising catalyst.
2. A process according to claim 1, in which

- the organo-metallic compound is selected from magnesium alkyls, magnesium aryls, zinc alkyls and zinc aryls.
3. A process according to claim 1, in which the organo-metallic compound is selected from the alkyl magnesium halides, aryl magnesium halides, alkyl zinc halides and aryl zinc halides.
4. A process according to claim 1, 2 or 3, in which the compound of a metal of the α sub-groups of Groups IV to VI of the Periodic Table is selected from salts of titanium, zirconium and chromium.
5. A process according to any of the preceding claims, in which the polymerisation is carried out at a pressure below 250 atmospheres.
6. A process as claimed in claim 5, in which the polymerisation is carried out at a pressure of 10 to 100 atmospheres.
7. A process as claimed in claim 5, in which the polymerisation is carried out at atmospheric pressure.
8. A process according to any of the preceding claims, in which the polymerisation is carried out at an elevated temperature.
9. A process according to claim 8, in which the polymerisation is carried out at a temperature between 50 and 250°C.
10. A process according to any of the preceding claims, in which the polymerisation is carried out in the presence of a solvent.
11. A process for the production of high molecular weight polyethylenes substantially as hereinbefore described.
12. High molecular weight polyethylenes when produced by the process claimed in any of the preceding claims.

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